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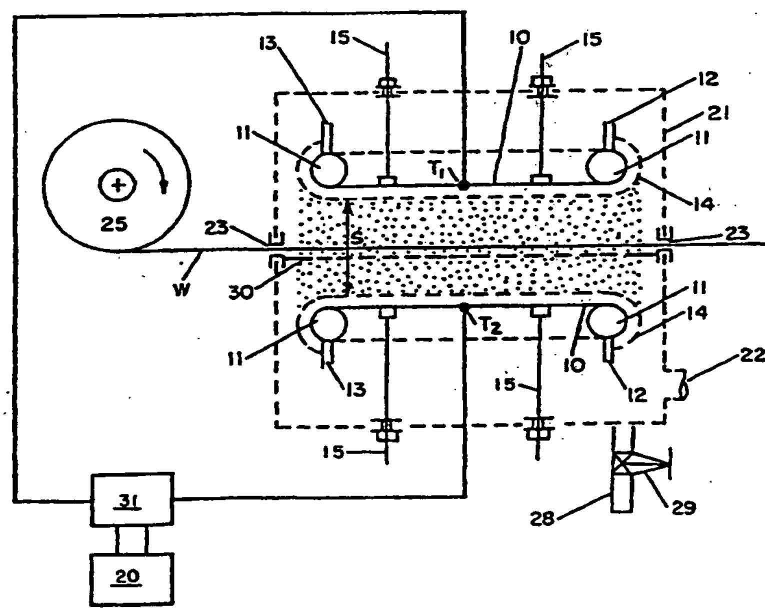

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(57) Abstract

A steady-state glow discharge plasma is generated at one atmosphere of pressure within the volume (S) between a pair of insulated metal plate electrodes (14) spaced up to 5 cm apart and rf energized with an rms potential of 1-5kV at 1-100kHz (20). Space between the electrodes is occupied by air, nitrous oxide, and a noble gas such as helium, neon, argon, etc., or mixtures thereof. The electrodes are charged by an impedance matching network (31) adjusted to produce the most stable, uniform glow discharge. Also, a method for treating a meltblown polymer web, using the aforementioned plasma device, is included.

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METHOD AND APPARATUS FOR GLOW DISCHARGE PLASMA TREATMENT OF POLYMER MATERIALS AT ATMOSPHERIC PRESSURE

BACKGROUND OF THE INVENTION

The present invention relates to a method and apparatus for modifying the surface properties of organic and inorganic polymer materials such as film and fabric, woven and non-woven.

One of the many utilities for meltblown polymer web is as a wet cell battery plate separator. The base polymer compound is impervious to the electrolyte. The meltblown, non-woven fabric structure is ion permeable if the surface thereof is thoroughly wetted by the electrolyte. Unfortunately, this latter requirement of wettability is not an inherent characteristic of most commercial polymers such as nylon, polypropylene, polyethylene and poly(ethylene terephthalate).

Although meltblown webs of these polymers are currently used as battery plate separators, wettability is achieved chemically by means of surfactants. This process not only generates hazardous industrial waste but produces a product of limited utility life.

Wettability is also a desirable property for tissue and cloth used to wipe or clean the body, for surgical sponges, wound dressings, feminine hygiene products and reusable woven knit fabrics. Similarly, wettability is an important material surface property for printing and laminating.

Some success has been recently achieved by a glow discharge plasma treatment of polymer webs. The term "plasma" usually describes a partially ionized gas composed of ions, electrons and neutral species. This state of matter may be produced by the action of either very high temperatures, or strong direct current (DC) or radio frequency (RF) electric fields. High temperature or "hot"

plasmas are represented by celestial light bodies, nuclear explosions and electric arcs. Glow discharge plasmas are produced by free electrons which are energized by an imposed DC or RF electric field and then collide with neutral molecules. These neutral molecule collisions transfer energy to the molecules and form a variety of active species which may include photons, metastables, individual atoms, free radicals, molecular fragments, monomers, electrons and ions. These active species are chemically active and/or capable of physically modifying the surface and may therefore serve as the basis of new surface properties of chemical compounds and property modifications of existing compounds.

Low power plasmas known as dark discharge coronas have been widely used in the surface treatment of thermally sensitive materials such as paper, wool and synthetic polymers such as polyethylene, polypropylene, polyolefin, nylon and poly(ethylene terephthalate). Because of their relatively low energy content, corona discharge plasmas can alter the properties of a material surface without damaging the surface.

Glow discharge plasmas represent another type of relatively low power density plasma useful for non-destructive material surface modification. These glow discharge plasmas can produce useful amounts of visible ultraviolet radiation. Glow discharge plasmas have the additional advantage therefore of producing visible and UV radiation in the simultaneous presence of active species. However, glow discharge plasmas have heretofore been successfully generated typically in low pressure or partial vacuum environments below 10 torr which may necessitate batch processing and the use of expensive vacuum systems. Several polymer species exposed to low pressure glow discharge plasmas respond with enhanced surface wettability characteristics. However, the chemical/physical mechanisms

are not understood and the characteristic is lost upon drying. Rewettability remains elusive.

The generation of low power density plasmas at one atmosphere is not new. Filamentary discharges between parallel plates in air at one atmosphere have been used in Europe to generate ozone in large quantities for the treatment of public water supplies since the late 19th century. Such filamentary discharges, while useful for ozone production, are of limited utility for the surface treatment of materials, since the plasma filaments tend to puncture or treat the surface unevenly.

It is an object of the present invention, therefore, to provide a non-byproduct producing process for enhancing the wettability of meltblown polymer webs and other types of polymeric substrates.

Another object of the invention is to teach a glow discharge plasma process for treating polymer web or film that provides a stable, rewettable product.

Another object of the invention is to provide a method and apparatus for continuously processing a polymer web or film of indefinite length through a glow discharge plasma at atmospheric pressure and standard temperature.

A still further object of the present invention to teach the construction and operating parameters of a glow discharge plasma having operability in an environmental pressure of about one atmosphere or slightly greater.

<u>INVENTION SUMMARY</u>

The present invention provides as a product an improved web, preferably a meltblown polymer web, having a surface enhanced by exposure to a sustained atmospheric, glow discharge plasma. The invention also includes a process specially adapted for the manufacture of said web product, and apparatus specifically designed for carrying out said process.

The above and other objects of the invention to be subsequently explained or made apparent are accomplished with an apparatus based upon a pair of electrically insulated metallic plate electrodes which may or may not have a median plate or screen between them. These plates are mounted in face-to-face parallel or uniformly spaced alignment with means for reciprocatory position adjustment up to about 5 cm of separation. Preferably, the plates are water cooled and covered with a dielectric insulation.

To broaden the range of operating frequency and other parameters over which the desirable uniform (as opposed to filamentary) glow discharge is observed, an impedance matching network is added to the circuit for charging the electrodes. The parameters of such a matching network are adjusted for the most stable, uniform operation of the glow discharge. This condition can occur when the reactive power of the plasma reactor is minimized.

A radio frequency power amplifier connected to both plates delivers at least 180 watts of reactive and plasma power at a working voltage of 1 to at least 5 kV rms and at 1 to 100 kHz.

To assist the starting of the plasma, the electrical discharge from a standard commercial Tesla coil may be briefly applied to the volume between the R.F. energized plates. An electric field established between the metallic plate electrodes must be strong enough to electrically break down the gas used, and is much lower for helium and argon than for atmospheric air. The RF frequency must be in the right range, discussed below, since if it is too low, the discharge will not initiate, and if it is too high, the plasma forms filamentary discharges between the plates. Only in a relatively limited frequency band will the atmospheric glow discharge plasma reactor form a uniform plasma without filamentary discharges.

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At least in the volume between the plates wherein the plasma is established, a one atmosphere charge of air, helium or argon is established and maintained for processing material such as polymer film and web to produce desired surface characteristics such as wettability and re-wettability.

BRIEF DESCRIPTION OF THE DRAWINGS

Relative to the drawings wherein like reference characters designate like or similar elements throughout the several figures of the drawings:

Figure 1 is a schematic of the present invention component assembly.

Figure 2 is an impedance matching network distinctively suitable for powering the present invention.

Figures 3, 4 and 5 are representative alternative power supply output stage circuits.

Figure 6 schematically represents an alternative embodiment of the invention.

Figure 7 schematically represents the upper chamber of a one atmosphere glow discharge plasma reactor having a median grid plate.

Figure 8 represents a graph of voltage, current and power waveforms for a uniform glow discharge plasma.

Figure 9 represents a graph of voltage, current and power waveforms for a filamentary discharge plasma.

Figure 10 is a log-log graph of total and plasma power density in milliwatts per cubic centimeter, as functions of RMS voltage applied to the electrodes.

Figure 11 is a log-log graph of total and plasma power density in milliwatts per cubic centimeter, as functions of R.F. frequency.

Figure 12 is a graph of amplifier frequency and corresponding breakdown current phase angles respective to a particular operating example of the invention.

Figure 13 is a graph of amplifier frequency and corresponding power consumption respective to a particular operating example of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the invention schematic illustrated by Figure 1, the electrodes 10 are fabricated of copper plate having a representative square plan dimension of 21.6 cm x 21.6 cm. Silver soldered to the plates 10 are closed loops 11 of 0.95 cm copper tubing having hose nipples 12 and 13 connected therewith on opposite sides of the closed tubing loop. The edges of the electrode plates should have a radius of curvature comparable to the separation between the electrode plates and median plate to discourage electrical breakdown at the edge of the electrodes. Not shown are fluid flow conduits connected to the inlet nipples 12 for delivering coolant fluid to the loop 11 and to the outlet nipples 13 for recovering such coolant fluid.

The integral metallic units comprising plates 10 and tubing 11 are covered with a high dielectric insulation material 14 on all sides to discourage electrical arcing from the edges or back side of the electrode plates.

Preferably, some mechanism should be provided for adjusting the distance s between plates 10 up to about 5 cm separation while maintaining relative parallelism. Such a mechanism is represented schematically in Figure 1 by the rod adjusters 15 secured to the upper and lower plates 10.

This arrangement anticipates a positionally fixed median plate 30.

Although parallelism is used in the context of parallel planes, it should be understood that the terms also comprises non-planar surfaces that are substantially equidistant. Also included are the geometry characteristics of a cylinder having an axis parallel to another cylinder or to a plate.

Energizing the plates 10 is a low impedance, high voltage, R.F. power amplifier 20 having independently variable voltage and frequency capacities over the respective ranges of 1 to at least 5 kV and 1 to 100 kHz. Between the RF power supply 20 and the plates 10 may be an impedance matching network 31, described in greater detail relative to Figure 2.

Surrounding the plate assembly is an environmental isolation barrier 21 such as a structural enclosure suitable for maintaining a controlled gas atmosphere in the projected plan volume between the plates 10. Inlet port 22 is provided to receive an appropriate gas such as air, helium or argon, mixtures of helium or argon with oxygen or air or a mixture of argon with helium. In any case, gas pressure within the isolation barrier 21 is substantially ambient thereby obviating or reducing the need for gas tight seals. Normally, it is sufficient to maintain a low flow rate of the modified atmospheric pressure gas through the inlet port 22 that is sufficient to equal the leakage rate. Since the pressure within the isolation barrier 21 is essentially the same as that outside the barrier, no great pressure differential drives the leakage rate. A vent conduit 28 controlled by valve 29 is provided as an air escape channel during initial flushing of the enclosure. Thereafter, the valve 29 may be closed for normal operation.

Narrow material flow slits 23 are provided in the isolation barrier 21 to accommodate passage of a material

web W between the plates 10 as drawn from a supply reel 24 onto a rewind reel 25. Drive for the reels 24 and 25 is controlled to provide a predetermined residence time between the plates 10 and within the plasma for any given web element.

To broaden the range of operating frequency and other parameters over which the desirable uniform (as opposed to filamentary) glow discharge occurs, an impedance matching network, one embodiment of which is illustrated schematically by Figure 2, is added to the power circuit for charging the electrodes 10. The parameters of this matching network are adjusted for the most stable, uniform operation of the glow discharge. This condition can occur when the reactive power of the plasma reactor is minimized.

Figures 3 through 5 represent alternative power supply options having respective attractions. Figures 3 corresponds to a configuration wherein the bottom electrode terminal T_1 is connected to ground potential and the top terminal T_2 is charged at the full working potential. Figures 4 and 5 are electrical equivalents wherein the T_1 and T_2 voltages are 180° out of phase but at only half the maximum potential. Figure 4 represents a grounded center tap transformer whereas Figure 5 represents a solid state power circuit embodiment.

Shown in Figure 6 are two optional embodiments, the functions of which are to drive a reciprocating gas flow containing active species from the plasma back and forth through the web W. This can be accomplished either by a bellows 35 actuated by a reciprocating shaft 33, or by a piston 36 activated by a reciprocating shaft 32. The change in volume of the upper chamber will give rise to a periodic reversal of the pressure differential across the web W, hence, a periodic reversal of the gas flow. As an alternative embodiment, a passageway from behind the piston can be connected to the lower chamber as shown in the dashed line piping 34.

The Figure 6 embodiment of the invention provides an electrically grounded screen 30 to support the web W as it is drawn between the opposite material flow slits 23. This configuration attenuates an accumulated electrical charge on the web and also structurally supports the traveling fabric web as a pressure differential membrane between an upper, gas inlet chamber and a lower, vent chamber. This swept flow differential assures an internal saturation of the web W by the gas containing active species from the plasma.

Electric fields employed in a one atmosphere, uniform glow discharge plasma reactor are only a few kilovolts per centimeter, values which, if D.C., would usually be too low to electrically break down the background gas. Gases such as helium and air will break down under such low electric fields, however, if the positive ion population is trapped between the two parallel or uniformly spaced electrodes, this greatly increasing their lifetime in the plasma, while at the same time the electrons are free to travel to the insulated electrode plates where they recombine or build up a surface charge. The most desirable uniform one atmosphere glow discharge plasma is therefore created when the applied frequency of the RF electric field is high enough to trap the ions between the median screen and an electrode plate, but not so high that the electrons are also trapped during a half cycle of the R.F. voltage. The electrons may be trapped by bipolar electrostatic forces.

If the RF frequency is so low that both the ions and the electrons can reach the boundaries and recombine, the particle lifetimes will be short and the plasma will either not initiate or form a few coarse filamentary discharges between the plates. If the applied frequency is in a narrow band in which the ions oscillate between the median screen and an electrode plate, they do not have time to reach either boundary during a half period of

oscillation and be carried for long times. If the more mobile electrons are still able to leave the plasma volume and impinge on the boundary surfaces, then the desirable uniform plasma is produced. If the applied RF frequency is still higher so that both electrons and ions are trapped in the discharge, then the discharge forms a filamentary plasma.

Without limiting our invention to any particular theory, we are disposed to a relationship between the electrode spacing, the RMS electrode voltage, and the applied frequency which results in trapping ions but not electrons between the two plates, and produces the desired uniform one atmosphere glow discharge plasma. On Figure 7 is a schematic of the upper chamber of the one atmosphere glow discharge plasma reactor. The lower boundary of this space is the midplane screen or base, the floating potential of which should remain near ground if the RF power supply output is connected as a push-pull circuit to the two electrodes with a grounded center tap. In the data reported herein, the median screen was grounded through an inductive current choke. In the configuration of Figure 7, a Cartesian coordinate system is applied as shown, with the applied electric field in the x-direction. The maximum amplitude of the electric field between the grounded median screen and the upper electrode is E_o, and the separation of the screen from the electrodes is the distance d. The median screen, with an exposed sample on it, is assumed not to allow ions through the median plane from the upper chamber to the lower, or vice-versa.

The electric field between the electrodes shown on Figure 7 is given by

$$E=(E_0 \sin\omega t, 0, 0). \tag{1}$$

It is assumed that the one atmosphere glow discharge operates in a magnetic field free plasma. The equation of motion for the ions or electrons between the two plates is

given by a Lorentzian model, in which the electrons and ions collide only with the neutral background gas and, on each collision, give up all the energy they acquired from the RF electric field since the last collision to the neutral gas. The equation of motion for the ions or electrons in the Lorentzian model is given by

$$F=ma=-mv_c v-eE, \tag{2}$$

where the first term on the right hand side is the Lorentzian collision term, according to which the momentum mv is lost with each collision that occurs with a collision frequency v_c. The x component of Eq. 2 is given by

$$m\frac{d^2X}{dt^2}+mv_c\frac{dx}{dt}=eE_o\sin\omega t, \tag{3}$$

where the electric field E from Eq. 1 has been substituted into the right hand side of Eq. 2. The general solution to Eq. 3 is

$$x=C_1\sin\omega t=C_2\cos\omega t, \tag{4}$$

where the constants C_1 and C_2 are given by

$$C_1=-\frac{eE_o}{m}\frac{1}{(\omega^2+v_c^2)}, \tag{5}$$

and

$$C_2=-\frac{v_c eE_o}{\omega m}\frac{1}{(\omega^2+v_c^2)} \tag{6}$$

The one atmosphere helium glow discharge is operated at frequencies between $\omega/2\pi$ = 1 and 30 kHz, where, for helium at one atmosphere,

$$v_{ci}\approx 6.8\times 10^9 \textit{ ion collisions/sec.}, \tag{7a}$$

and

$$\nu_{ce} \approx 1.8 \times 10^{12} \, electron\ coll./sec. \qquad (7b)$$

The collision frequency for ions and electrons given by Eqs. 7a and 7b is much greater than the RF frequency, $V_c >> \omega$. The relation $\nu_c >> \omega$ for ions and electrons, implies that C_2 is much greater than the constant C_1, or

$$C_2 \approx \frac{eE_o}{m\omega\nu_c} >> C_1 \qquad (8)$$

The time dependent position of an ion or an electron in the electric field between the plates is given by substituting Eq. 8 into Eq. 4, to obtain

$$x(t) \approx -\frac{eE_o}{m\omega\nu_c}\cos\omega t. \qquad (9)$$

The RMS displacement of the ion or electron during a half cycle is given by

$$x_{rms} = \frac{2}{\pi}\frac{eE_o}{m\omega\nu_c} meters. \qquad (10)$$

If V_o is the driving frequency, in Hertz, then the radian RF frequency is given by

$$\omega = 2\pi\nu_o, \qquad (11)$$

and the maximum electric field between the plates can be approximated by the maximum voltage V_o appearing between them,

$$E_o = \frac{V_o}{d} = \frac{\pi V_{rms}}{2d}. \qquad (12)$$

If the charge in question moves across the discharge width from the median plane to one of the electrode plates during one full cycle, then we may write

$$x_{rms} \lesssim \frac{d}{2}. \qquad (13)$$

Equation 13 states that the RMS displacement of the particle has to be less than half the clear spacing in order to have a buildup of charge between the plates. In the geometry shown in Figure 7, the distance d is identified with the distance between the grounded median screen and the energized electrode. Substituting Eqs. 11 to 13 into Eq. 10 yields the relationship

$$\frac{d}{2} \approx \frac{eV_{rms}}{2\pi m v_o v_c d}. \qquad (14)$$

If we now solve for the critical frequency v_o above which charge buildup should occur in the plasma volume, we have

$$v_o \approx \frac{eV_{rms}}{\pi m v_c d^2} Hz. \qquad (15)$$

In Eq. 15, the collision frequency v_c is approximately given by Eqs. 7a or 7b for ions or electrons, respectively, at one atmosphere, and the RMS voltage is that which bounds the upper and lower limit of the uniform discharge regime.

The range of parameters over which we have operated a one atmosphere, uniform glow discharge plasma reactor is given in Table 1. The nominal pressure at which this discharge has been operated is one atmosphere. The variation of several torr shown in Table 1 is not intended to represent the day-to-day fluctuations of barometric pressure, but the pressure differential across the midplane screen which is intended to drive active species from the upper plasma through the fabric being exposed. The RMS power shown in Table 1 is the net power delivered to the plasma, less the reactive power which does not appear in the plasma. The total volume of plasma between the two electrode plates is given by

$$S=0.93\ d(cm)\ liters, \tag{16}$$

where d is the separation of a plate from the median screen in centimeters.

The power densities shown in Table 1 are far below those of electrical arcs or plasma torches, but also are several orders of magnitude higher than the power densities associated with some other forms of plasma treatment such as corona discharges. The power densities of the one atmosphere glow discharge plasma are generally low enough not to damage exposed fabrics, but are also enough higher than coronal plasmas used for surface treatment that they should provide far more active species than the latter. The plasma parameters, such as electron kinetic temperature and number density are somewhat speculative at this early stage in the development of our invention. A few results from probing the plasma midplane with a floating Langmuir probe indicates that the plasma, without grounding the midplane screen, will float to positive potentials of several hundred volts. The ion kinetic temperatures are very likely close to that of the room temperature atoms with which they frequently collide at these high pressures; the electrons apparently remain numerous and energetic enough to excite the neutral background atoms, hence making this a glow discharge. The existence of excited states which emit visible photons implies that the electron population has a kinetic temperature of at least an electron volt. The diagnostic difficulties of measuring plasma parameters at this high pressure are very severe, since ordinary Langmuir probing technique cannot be applied due to the short mean free paths of the electrons compared to a Debye distance. Electron number densities, however, may be measured by microwave interferometric techniques.

TABLE 1

OPERATING CHARACTERISTICS OF THE ONE ATMOSPHERE GLOW DISCHARGE PLASMA REACTOR

working gas = He, He + 1-7% O_2, Ar, Ar + He, Ar + 1-7% O_2, and atmospheric air
frequency = 1 kHz to 100 kHz
voltage = 1.5 - 9.5 kV_{rms} plate to plate
electrode gap d = 0.8 - 3.2 cm
pressure = 760 +15, -5 torr
RMS power = 10 watts to 150 watts
power density = 4 - 120 mW/cm^3
plasma volume = 0.7 - 3.1 liters

On Figures 8 and 9 are shown two waveforms of voltage and current taken in helium at the same electrode separation and gas flow conditions, but at two different frequencies. Figure 8 was taken in the uniform glow discharge regime at a frequency of 2.0 kHz, and Figure 9 was taken in the filamentary discharge regime at a frequency above the uniform plasma operating band at 8.0 kHz. The high output impedance of our RF power supply results in a voltage waveform (trace B) that is very close to sinusoidal. The reactive current waveform (trace C) is interrupted by a breakdown of the plasma twice each cycle, once when the voltage is positive, and once when the voltage is negative. Trace A shows the reactive current waveform at the same voltage and operating conditions, but in air, rather than helium. There was no perceptible plasma present in air under these conditions, and the power is completely reactive. This purely reactive current of trace A was subtracted from the total plasma current in trace C, to yield trace D. The instantaneous power deposited in the plasma (trace E) is found by multiplying the excess plasma current above the reactive current (trace

D) by the voltage at that point (trace B). The average power is found by integrating over the duration of the pulses shown, and dividing by this duration. It is in this manner that the power and power density into the plasma were calculated for these highly nonsinusoidal current waveforms. Figures 8 for the uniform discharge and 9 for the filamentary discharge show characteristically different power waveforms in trace E; this is a method of distinguishing the uniform from the filamentary discharge.

The plasma power is of interest because it is proportional to the production rate of active species in the plasma; the reactive power is significant because it determines the required power handling rating of the plasma power supply and associated equipment. The total power is the sum of plasma and reactive power. On Figure 10 is shown a log-log plot of the plasma and total power density in milliwatts per cubic centimeter, as functions of the RMS voltage applied to the parallel plates. The active plasma volume in Figure 10 was 1.63 liters, with a separation between the median screen and each plate of d = 1.75 centimeters in a plasma of helium gas. On Figure 11 is a similar presentation of the power density plotted on log-log coordinates as a function of the frequency. The approximate bound of the uniform plasma discharge regime is shown by the arrow. These data were taken in helium gas for the same plasma volume and electrode separation as Figure 10.

<u>EXAMPLE 1</u>

In a first operational example of the invention, the Figure 1 described physical apparatus sustained a glow discharge plasma in one atmosphere of helium at standard temperature with a separation distance s of 3.0 cm between plates 10. The plates were energized with a 4.4 kV rms working potential. Holding these parameters constant, R.F. frequency was increased as an independent variable. As the dependent variable, Figure 12 charts the corresponding

breakdown current phase angle as determined relative to the voltage waveform node. Similarly, Figure 13 charts the total power, including reactive and plasma input power required to sustain the plasma at the respective R.F. frequencies.

EXAMPLE 2

In a second operational example of the invention, the Figure 1 described physical apparatus is used to sustain a glow discharge plasma in one atmosphere of helium at standard temperature with a separation distance s of 1.0 cm between plates 10. In this example, the R.F. frequency was held constant at 30 kHz while plate potential was manipulated as the independent variable and current breakdown phase angle, Θ, (Table 2) and total power, P, (Table 3) measured as dependent variables.

Table 2

V(kV)	1	1.5	2	2.5	3	3.5
Θ(deg)	28	40	61	46	65	76.5

Table 3

V(kV)	1	1.5	2	2.5	3	3.5
P(W)	7	13	22	57	50	44.9

EXAMPLE 3

A third operational example of the invention included a one atmosphere environment of helium between a 1 cm separation distance s between plate electrodes 10 charged at 1.5 kV rms potential. The R.F. frequency was manipulated as the independent variable. As a measured dependent variable, Table 4 reports the corresponding phase angle Θ of breakdown current. The measured dependent variable of Table 5 reports the corresponding total power consumption data.

Table 4

f(kHz)	10	20	30	40	50	60	70	80	90	100
Θ(deg)	43	32	43	52	54	61	60	56	45	22.5

Table 5

f(kHz)	10	20	30	40	50	60	70	80	90	100
P(W)	5	8	11	19	35	43	47	57	89	124

EXAMPLE 4

The largest volume helium plasma of 3.1 liters was achieved with the above described apparatus at a 3.2 cm plate separation having a 5 kV rms potential at an R.F. frequency of 4 kHz.

Meltblown webs formed from nylon, poly(ethylene terephthalate), polypropylene and polyethylene have been processed by exposure to the glow discharge plasma described herein to produce desired material characteristics, increased wettability and re-wettability.

Wettability of a material is objectively measured by either or both of two tests including (a) the angle of a water bead supported on the material surface and (b) the time required to wick along a predetermined material length.

By such tests, it was determined that polypropylene, nylon, polyester and polyethylene film experienced a significant wettability and re-wettability improvement after a 2.5 minute plasma exposure as evidenced by a greatly reduced bead angle.

A poly(ethylene terephthalate) web, after 2.5 minutes of glow discharge plasma exposure to a 5kV, 4kHz across a 4.5 cm plate separation, experienced a 0° surface bead angle and a 37.37 second wicking rate determined by the INDA standard absorption test. Prior to plasma exposure, the web had a large surface bead angle and no wicking capacity.

Similarly, after only 60 seconds of exposure to the same plasma, a nylon web, having a high surface bead angle and no wicking capacity enjoyed a 0° surface bead angle and a 16.61 second wicking rate (INDA standard test) upon wetting and re-wetting.

In another test set, two different meltblown webs poly(ethylene terephthalate) and polypropylene (PET and PP), were treated by the one atmosphere glow discharge plasma with helium or helium plus active gases as the working gas for a treating time period of from one-half minute to two minutes. The power supply voltage was from 1,000 V_{rms} to 4,000 V_{rms} and the frequency was from 1 kHz to 100 kHz. The webs had a fiber size of 2 to 2.5 microns, a pore size of 20-25 microns, and a porosity of 90%. Table 6 lists some initial results from these treatments.

Wettability was justified by contact angle, wickability, and wetout of the liquid through web thickness and on the web surface. Wickability was measured according to INDA standard (1st 10.1-92), in which time was measured for the liquid (double D's water) to rise 2.4 cm high. Physical fiber surface change was analyzed by photomicrographs taken using the ETEC Auto Scan electron microscope for a magnification of 2,000x to 4,000x.

TABLE 6

Treating Conditions				Wettability			
Sample	Time(s)	gases	kV_{rms}	Contact Angle	Wicking Rate(s)	Thickness Wettability	Surface Wettability
PP 0.35 oz	60	He, O_2	3.5	reduced	not sig.	90%	good
PP 0.35 oz	60	He, O_2	3.0	unchanged	no	75%	increased
PET 1 oz	90	He	2.3	0	31.74	good	good

Although expansive data is not presently available, it is to be noted that a uniform glow discharge plasma has been sustained by the Figure 1 apparatus with a one atmosphere ambient air environment and an 8 kV/cm electric field.

CLAIMS

1. A glow discharge plasma generation apparatus comprising a pair of electrically insulated electrodes energized by radio frequency (RF) amplifier means for energizing said electrodes with an impedance matching network having a potential of 1 to at least 5 kV rms at 1 to 100 kHz, said electrodes being aligned and secured in equidistant opposition with means to charge a volumetric space between said electrodes with a glow discharge plasma sustaining gas at a pressure of about 1 atmosphere,

wherein said apparatus comprises means to create and maintain a uniform 1 atmosphere glow discharge plasma by providing an applied frequency of the RF electric field which is high enough to trap the positive ions of the plasma between the electrodes, but not so high that the electrons of the plasma are also trapped during a half cycle of the RF voltage.

2. The apparatus of claim 1 wherein said means to charge said volumetric space between said plates comprises a gas barrier envelope surrounding said plates and the volumetric space therebetween.

3. The apparatus of claim 1 or 2 comprising gas supply means to maintain about one atmosphere of pressure within said envelope by a substantially steady supply flow of said gas.

4. The apparatus of any one of claims 1 to 3 wherein said gas is helium, argon, air or a mixture of any two thereof.

5. The apparatus of any one of claims 1 to 4 wherein said plates are fluid cooled.

6. The apparatus of claim 5 wherein fluid flow conduits are bonded to said plates to extract heat from said plates.

7. A method of generating a glow discharge plasma within a volumetric space between two electrodes

energized by radio frequency (RF) amplifier means having an impedance matching network, said method comprising the steps of operating said amplifier means to energize said electrodes with a potential of 1 to at least 5 kV rms at 1 to 100 kHz frequency and charging the volumetric space between said electrodes with a glow discharge plasma sustaining gas at approximately 1 atmosphere of pressure,

wherein a uniform 1 atmosphere glow discharge plasma is created and maintained by using an applied frequency of the RF electric field which is high enough to trap the positive ions of the plasma between the electrodes, but not so high that the electrons of the plasma are also trapped during a half cycle of the RF voltage.

8. The method of claim 7 wherein said electrodes are enclosed by an environmental gas barrier internally charged by a substantially continuous flow of said gas.

9. The method of claims 7 or 8 wherein said gas is helium, argon, air or a mixture of any two thereof.

10. The method of any one of claims 7 to 9 wherein said electrodes are positioned at a separation distance therebetween of 5 cm or less.

11. The method of claim 10 wherein at least one of said electrodes is positionally adjustable relative to the other.

12. The method of any one of claims 7 to 11 wherein said amplifier frequency is variable over the range of 1 to 100 kHz.

13. The method of any one of claims 7 to 12 wherein said amplifier potential is variable over the range of 1 to at least 5 kV rms.

14. A method for improving the surface characteristics of a web, the method comprising charging a glow discharge plasma sustaining gas to the volumetric space between a pair of spaced electrodes, generating a sustained, uniform glow discharge plasma having active

species between said electrodes, said electrodes being energized by radio frequency amplifier means over the range of about 1 to at least 5 kV rms at frequencies of about 1 to 100 KHz, and positioning said web between said electrodes and within said plasma for a predetermined period of time and pressure differentially driving said active species through said web.

15. The method of claim 14 wherein said gas is a noble gas.

16. The method of claim 14 wherein said gas is helium, argon, air or a mixture of any two thereof.

17. The method of any one of claims 14 to 16 wherein said web is a meltblown polymer web.

18. The method of any one of claims 14 to 17 wherein said frequencies are about 1 to 30 kHz.

19. The method of any one of claims 14 to 18 wherein said web is of indefinite length drawn between said electrodes at a substantially continuous rate to provide a predetermined elapsed residence time within said plasma.

20. A meltblown polymer web having a surface of enhanced wettability and re-wettability produced by a predetermined period of exposure to a sustained, atmospheric pressure, glow discharge plasma generated by radio frequency amplifier means operated at about 1 to at least 5 kV rms potential at about 1 to 100 kHz frequency.

21. The meltblown polymer web of claim 20 wherein said plasma is sustained by a noble gas.

22. The meltblown polymer web of claim 20 wherein said gas is helium, argon, air or a mixture of any two thereof.

23. The meltblown polymer web of any one of claims 20 to 22 formed from polypropylene.

24. The meltblown polymer web of any one of claims 20 to 23 where said frequency is about 1 to 30 kHz.

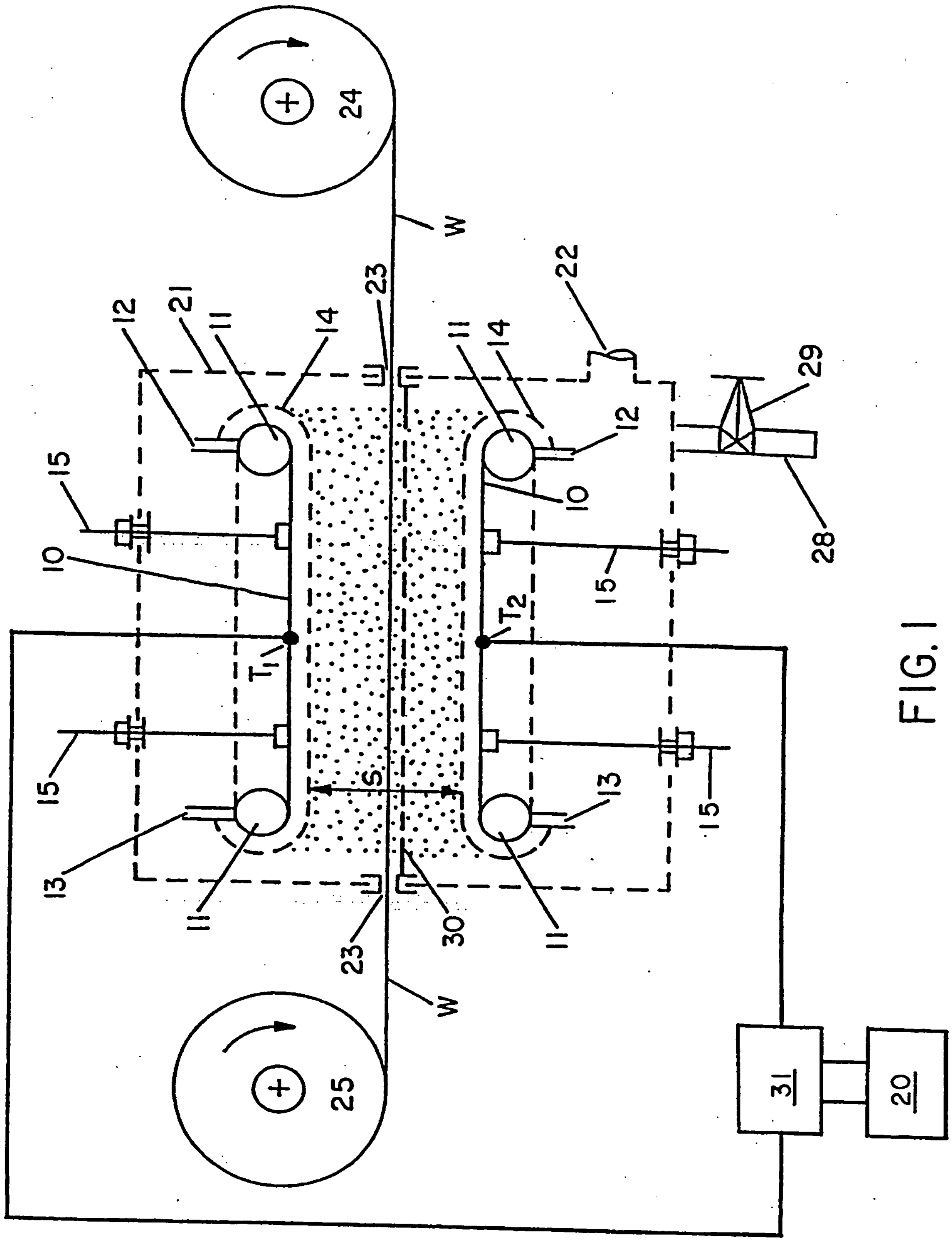

24
W
23
22
12
21
11
14
11
14
12
29
15
10
10
15
28
T2
T1
15
S
15
13
13
11
11
23
30
W
25
31
20

FIG. 1

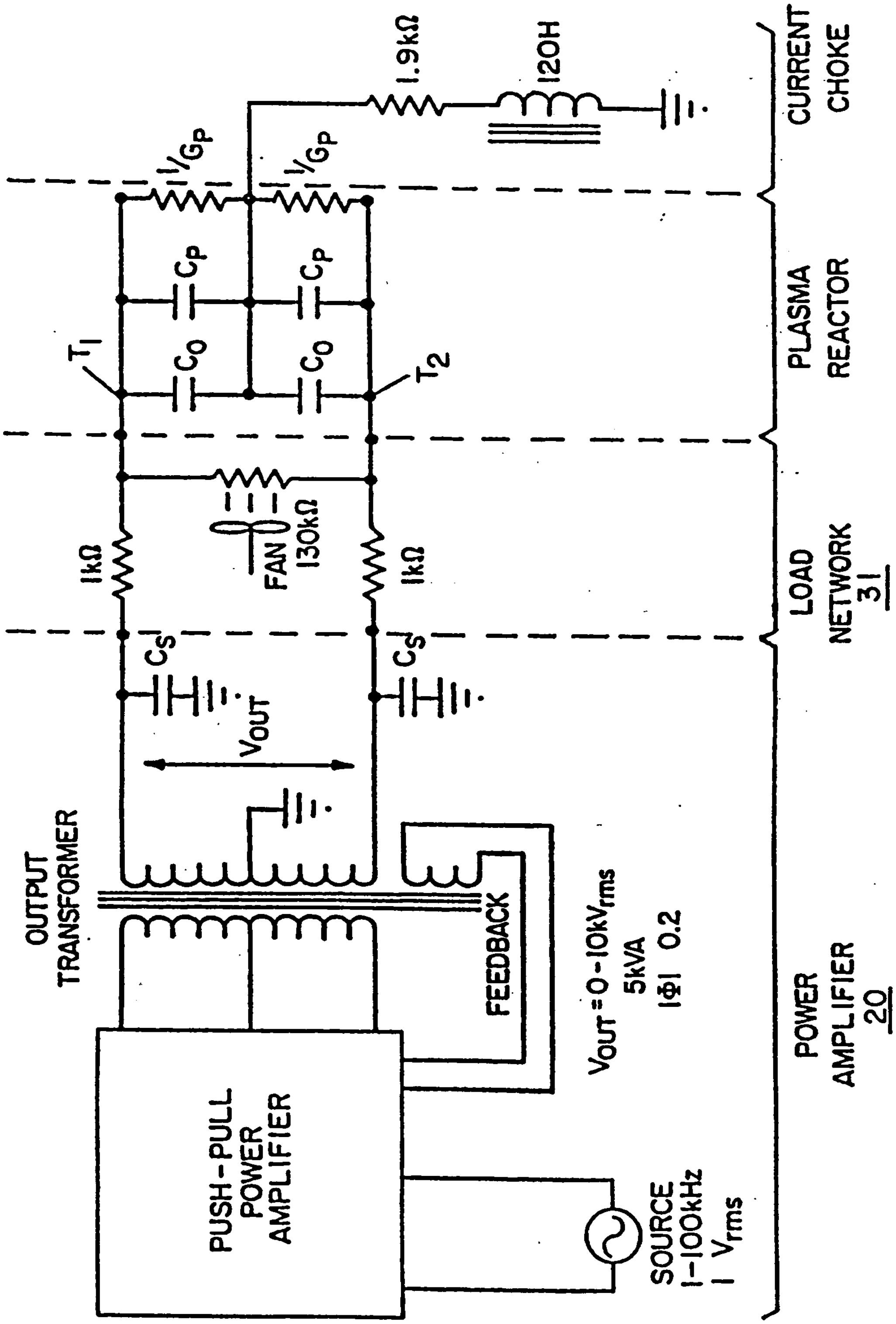

CURRENT
CHOKE
PLASMA
REACTOR
LOAD
NETWORK
31
POWER
AMPLIFIER
20
1.9kΩ
120H
1/GP
1/GP
CP
CP
CO
CO
T1
T2
1kΩ
1kΩ
FAN
130kΩ
CS
CS
VOUT
OUTPUT
TRANSFORMER
FEEDBACK
VOUT=0-10kVrms
5kVA
1Φ1 0.2
PUSH-PULL
POWER
AMPLIFIER
SOURCE
1-100kHz
1 Vrms

FIG. 2

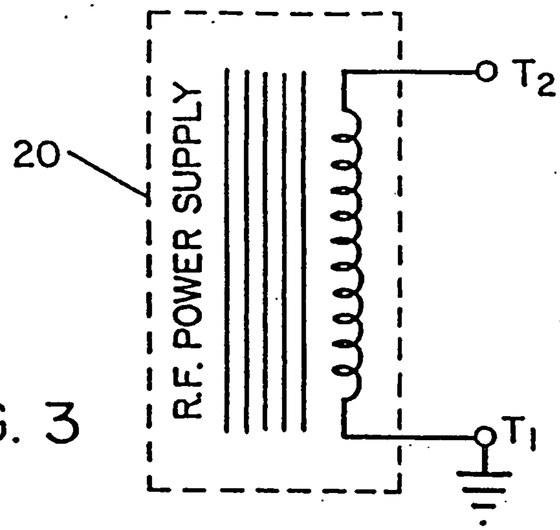


FIG. 3

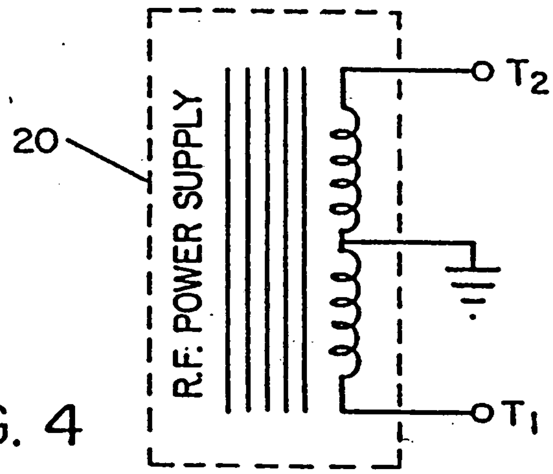


FIG. 4

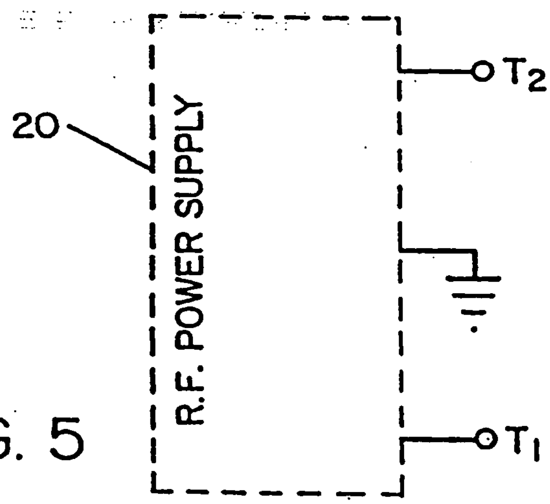


FIG. 5

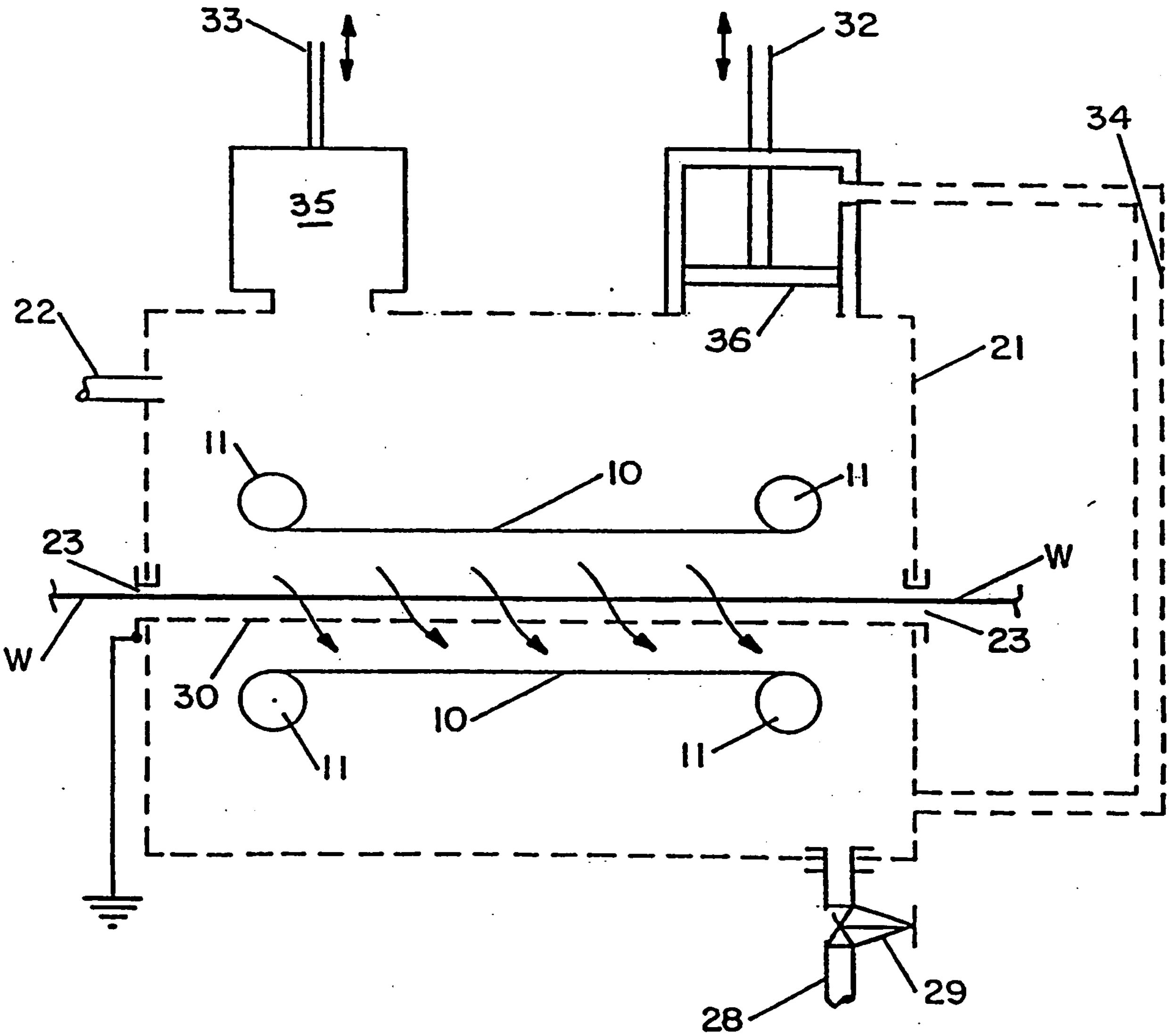


FIG. 6

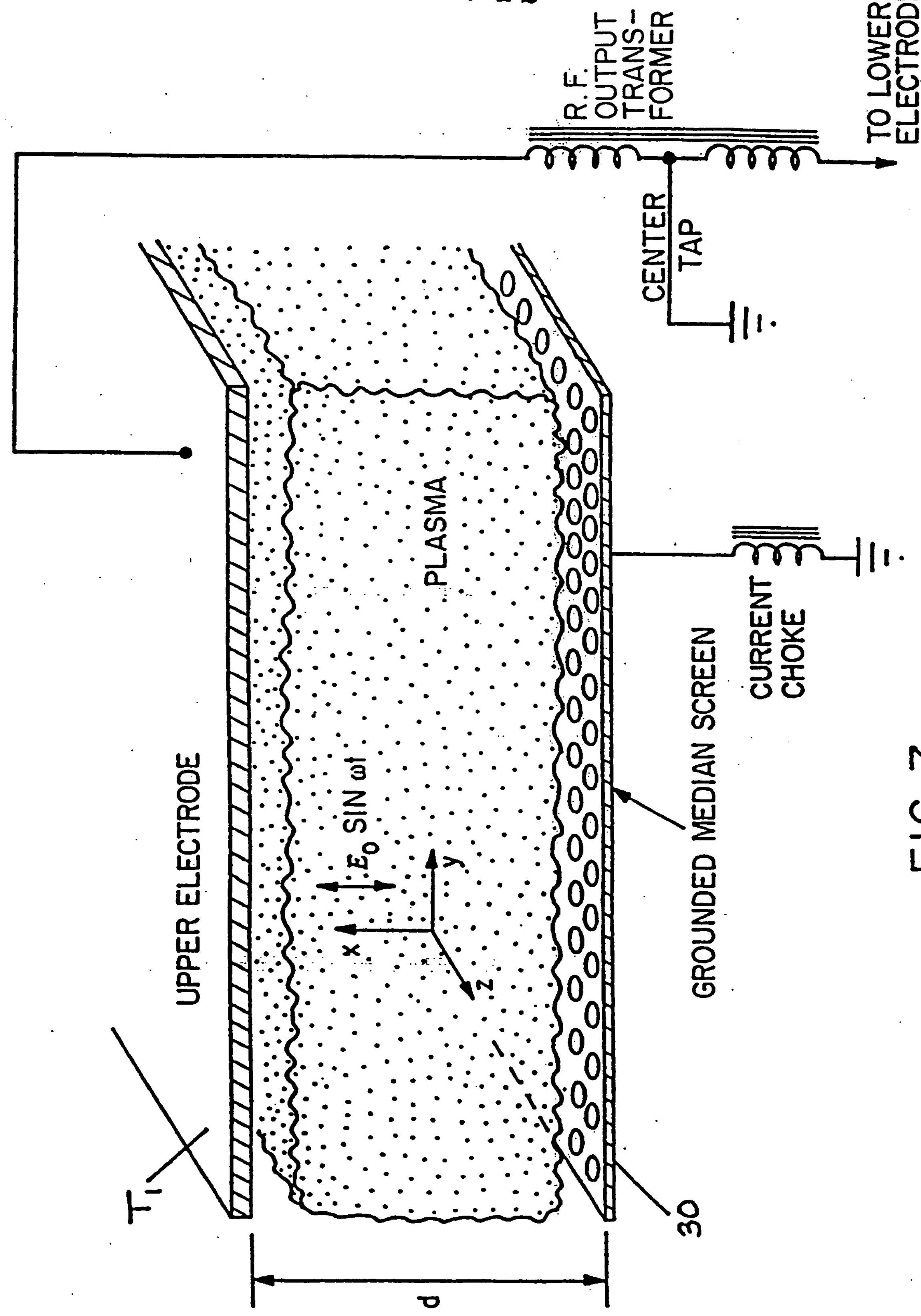

R.F. OUTPUT TRANS-FORMER
TO LOWER ELECTRODE
CENTER TAP
PLASMA
CURRENT CHOKE
GROUNDED MEDIAN SCREEN
UPPER ELECTRODE
E_0 SIN ωt
x
y
z
T_1
30
d

FIG. 7

FIG. 8A

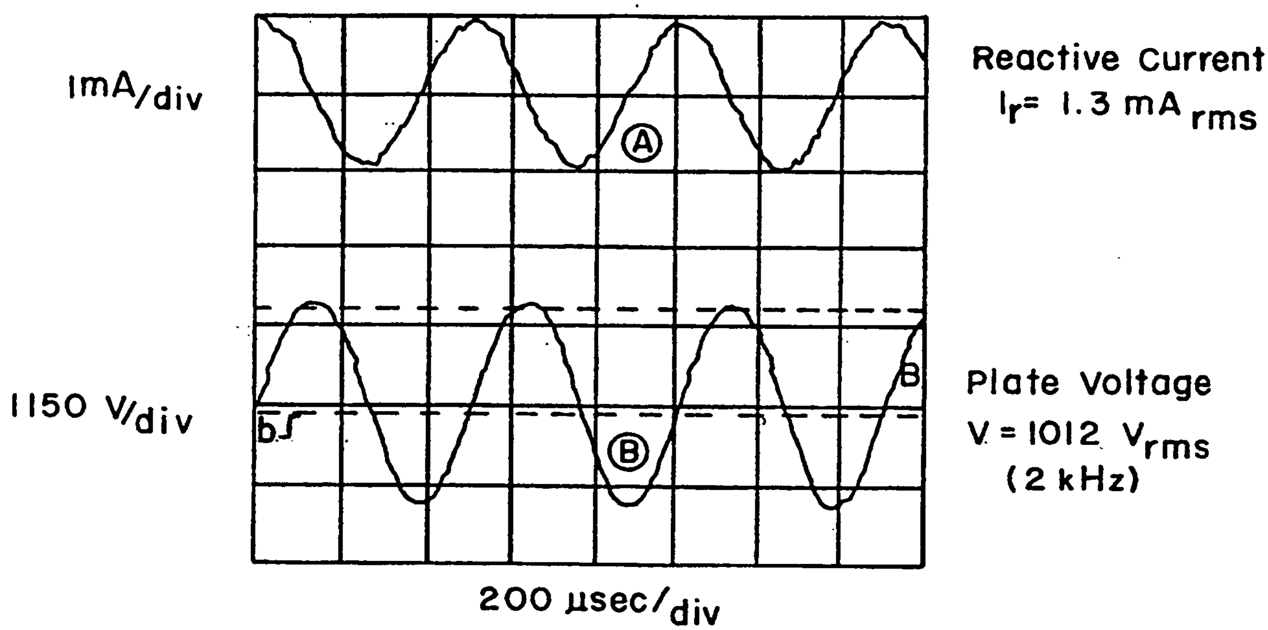

1mA/div
Reactive Current
I_r= 1.3 mA rms
A
1150 V/div
Plate Voltage
V = 1012 V_{rms}
(2 kHz)
B
b
200 µsec/div

FIG. 8B

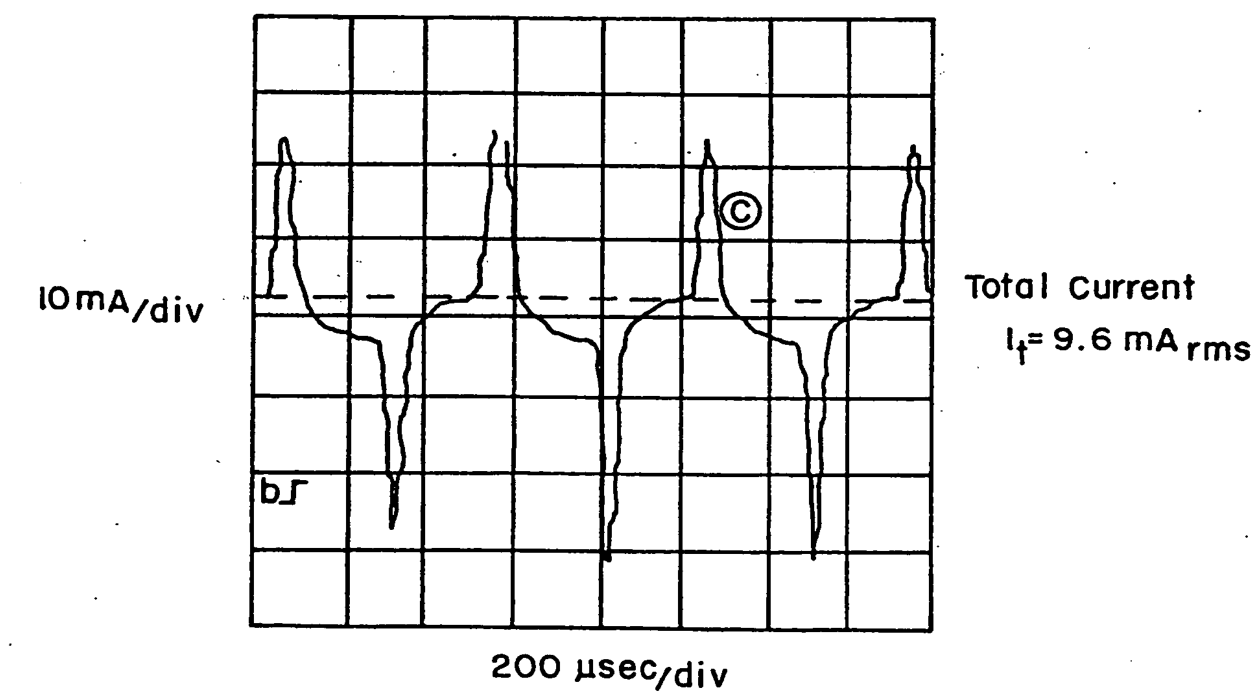

10mA/div
Total Current
I_t= 9.6 mA rms
C
b
200 µsec/div

FIG. 8C

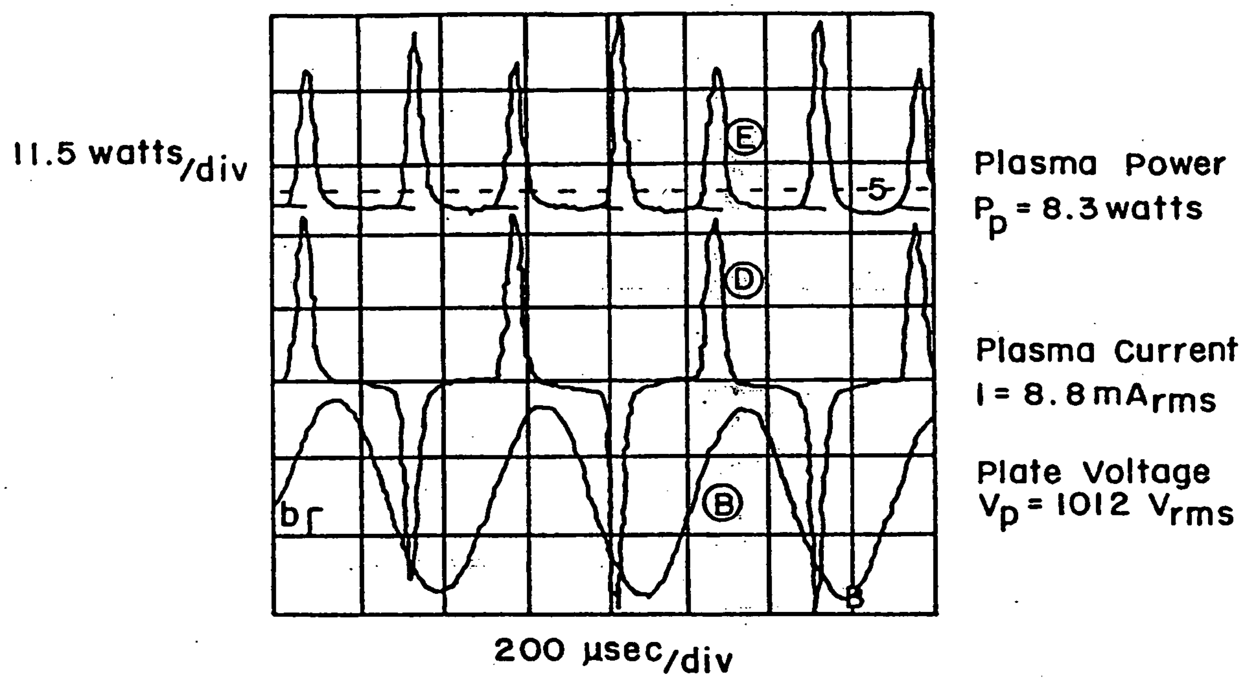

11.5 watts/div
Plasma Power
Pp = 8.3 watts
Plasma Current
I = 8.8 mArms
Plate Voltage
Vp = 1012 Vrms
E
D
B
b
-5-
B
200 μsec/div

FIG. 9A

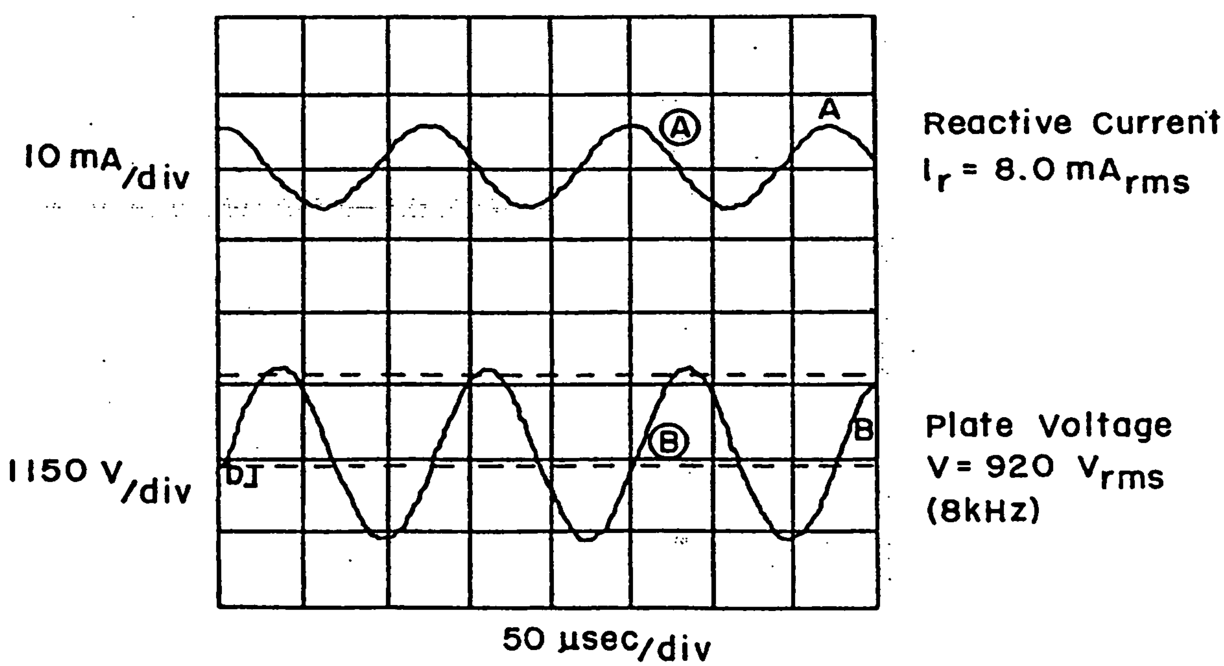
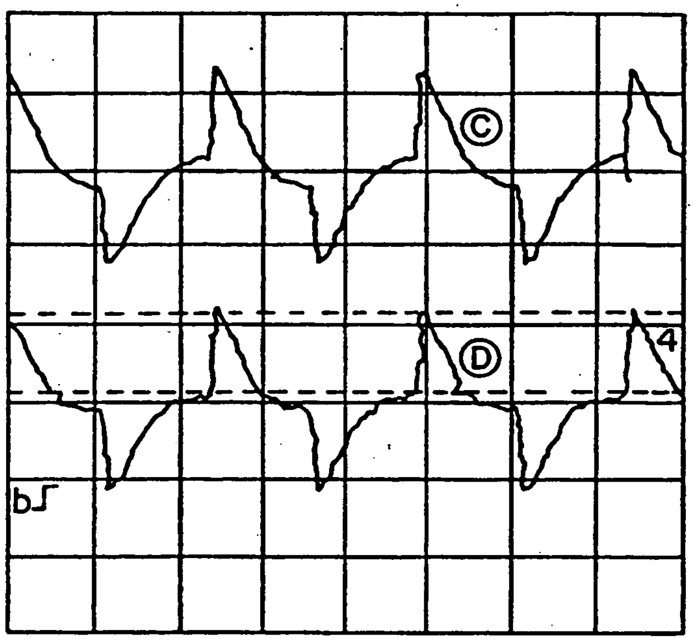

10 mA/div
Reactive Current
Ir = 8.0 mArms
1150 V/div
Plate Voltage
V = 920 Vrms
(8kHz)
A
A
B
B
b
50 μsec/div

FIG. 9B

50 mA/div



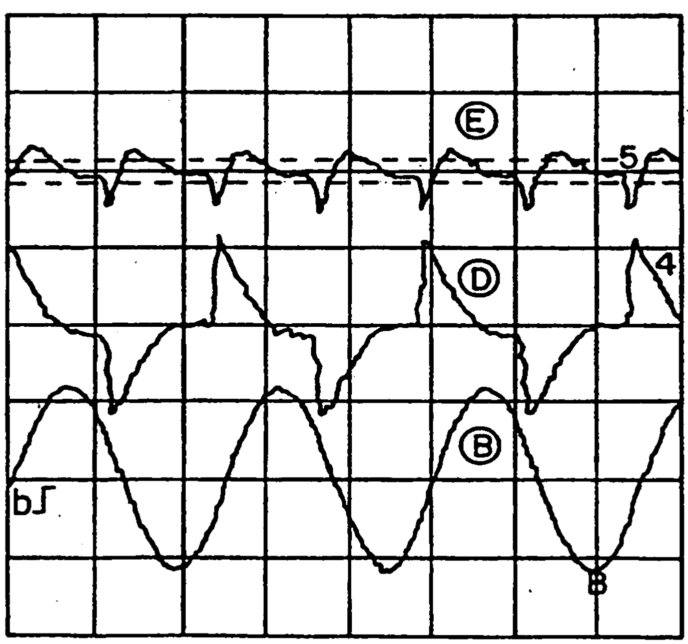
Total Current
I_t = 56 mA$_{rms}$

Plasma Current
I = 52 mA$_{rms}$

50 μsec/div

FIG. 9C

115 watts/div



Plasma Power
P_p = 18.4 watts

Plasma Current
I = 52 mA$_{rms}$

Plate Voltage
V = 920 V$_{rms}$

50 μsec/div

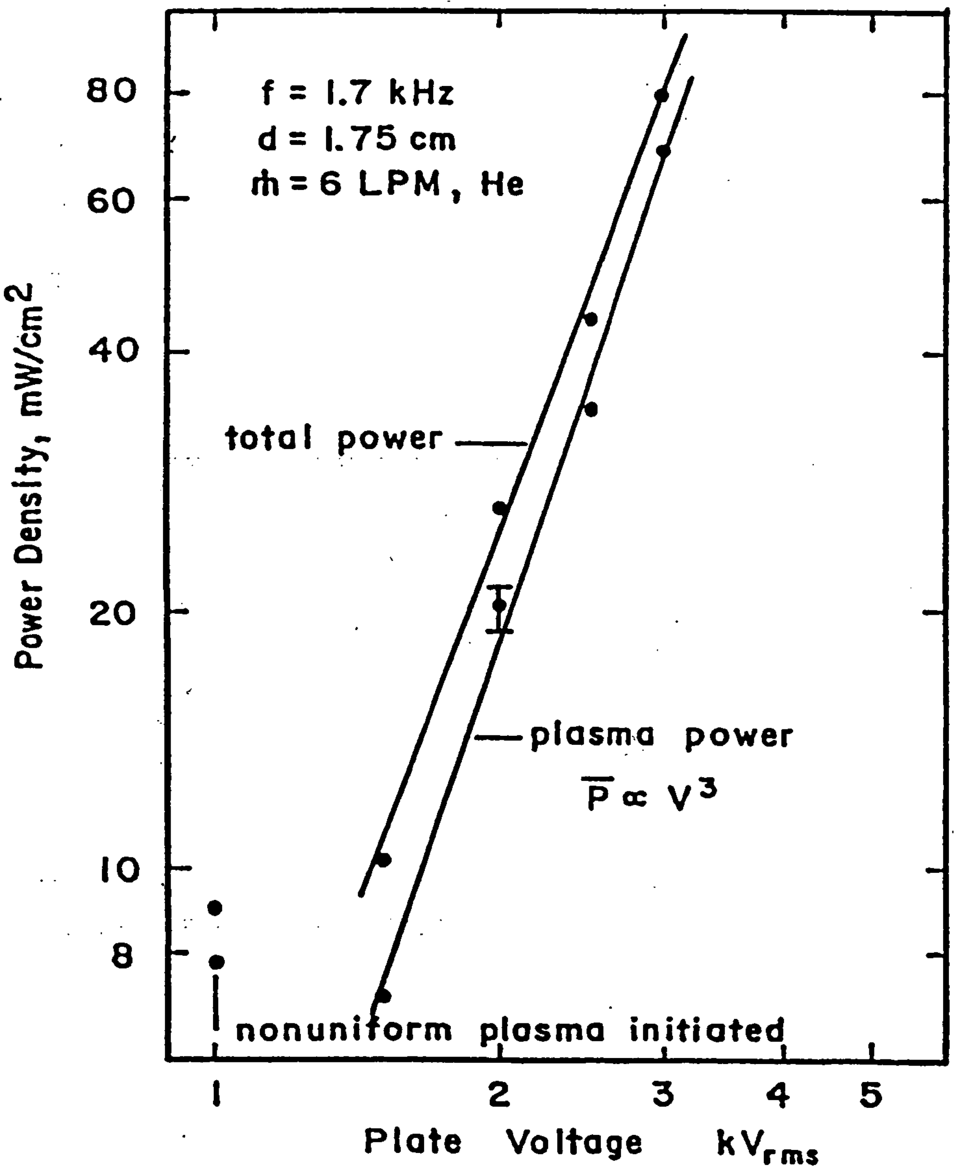
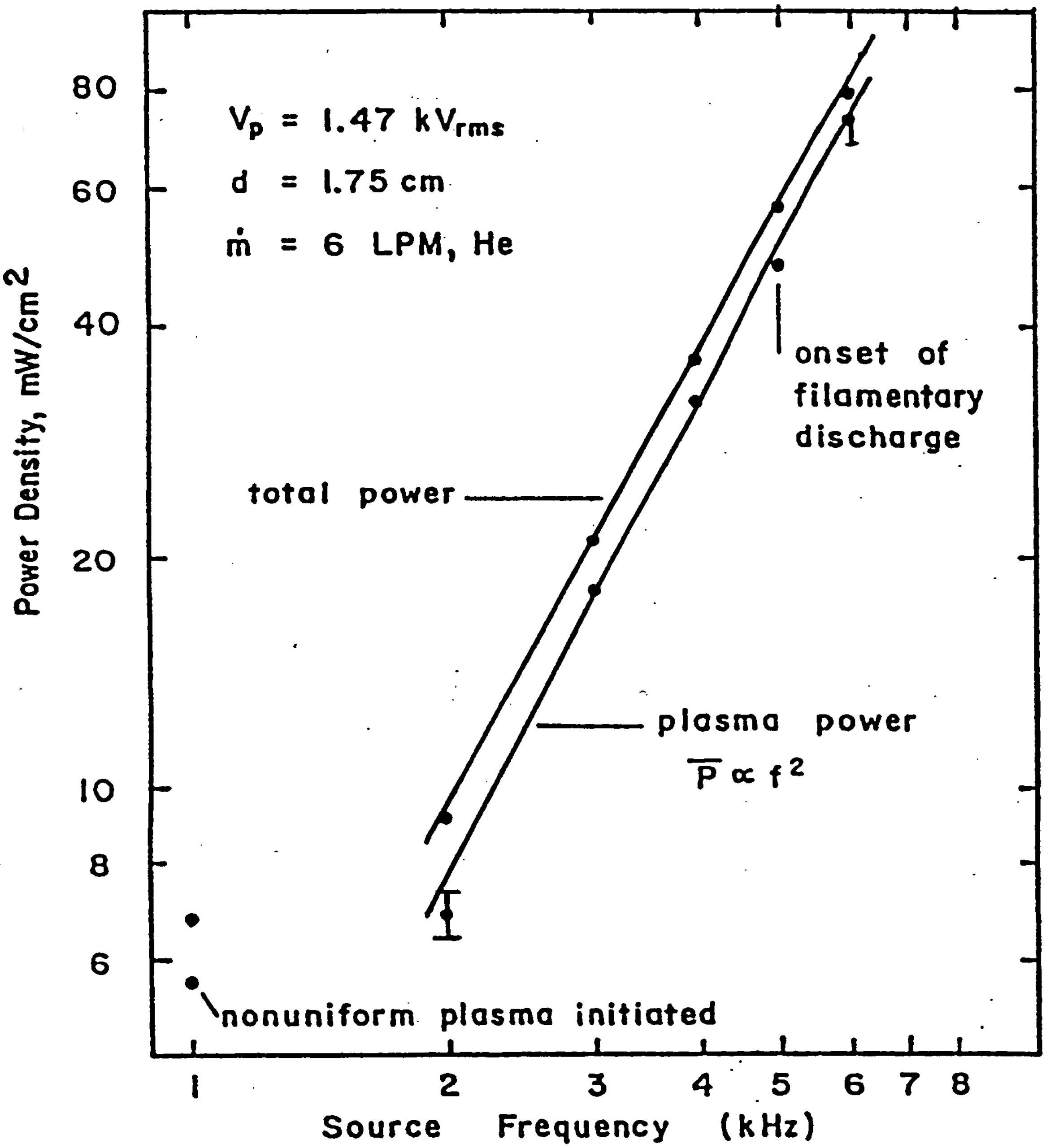

f = 1.7 kHz
d = 1.75 cm
ṁ = 6 LPM, He
80
60
40
20
10
8
Power Density, mW/cm^2
total power
plasma power
$\overline{P} \propto V^3$
nonuniform plasma initiated
1
2
3
4
5
Plate Voltage kV$_{rms}$

FIG. 10



80
60
40
20
10
8
6
Power Density, mW/cm2
Vp = 1.47 kVrms
d = 1.75 cm
m = 6 LPM, He
onset of filamentary discharge
total power
plasma power
P ∝ f2
nonuniform plasma initiated
1
2
3
4
5
6
7
8
Source Frequency (kHz)

FIG. 11

FIG. 12

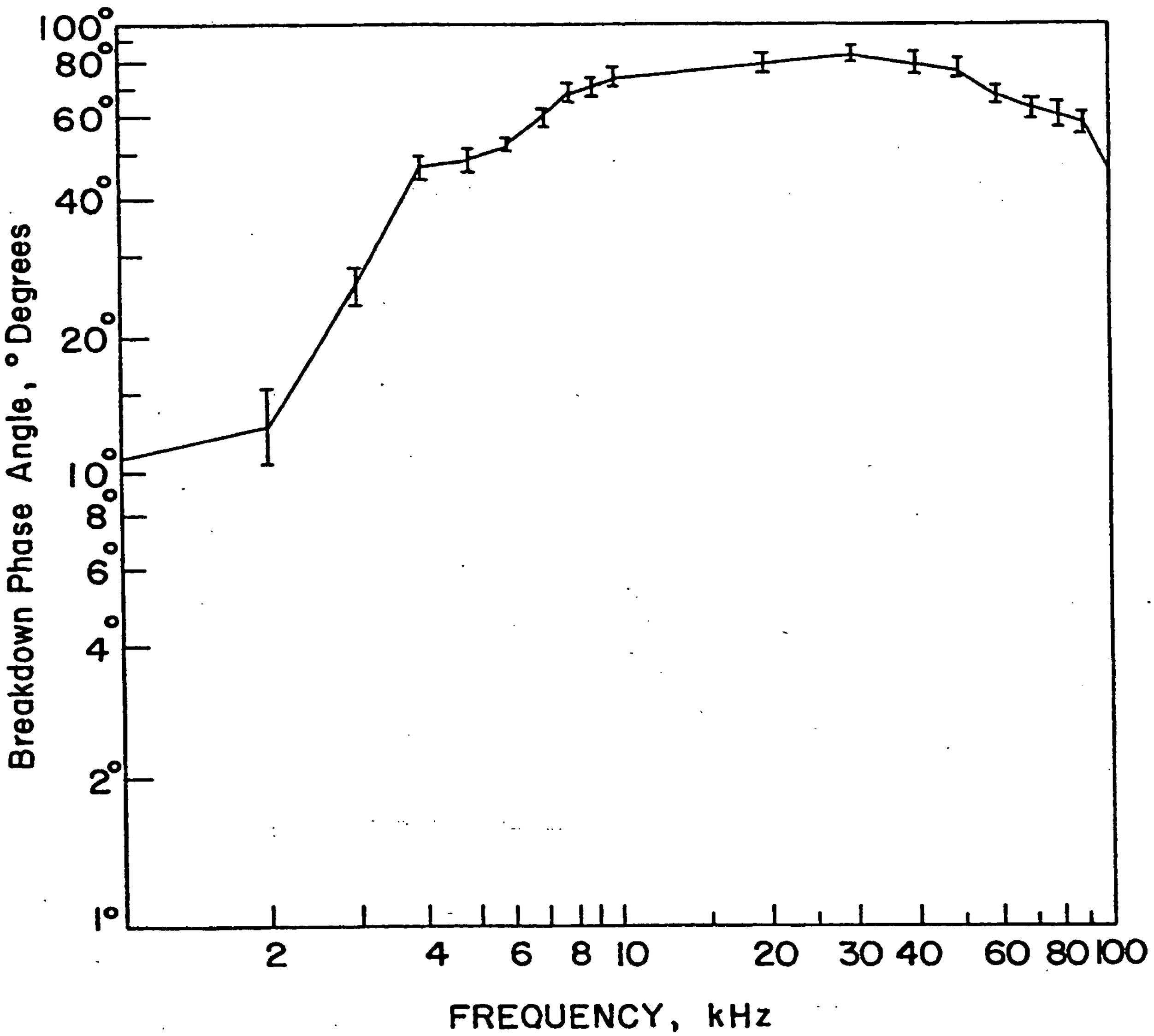
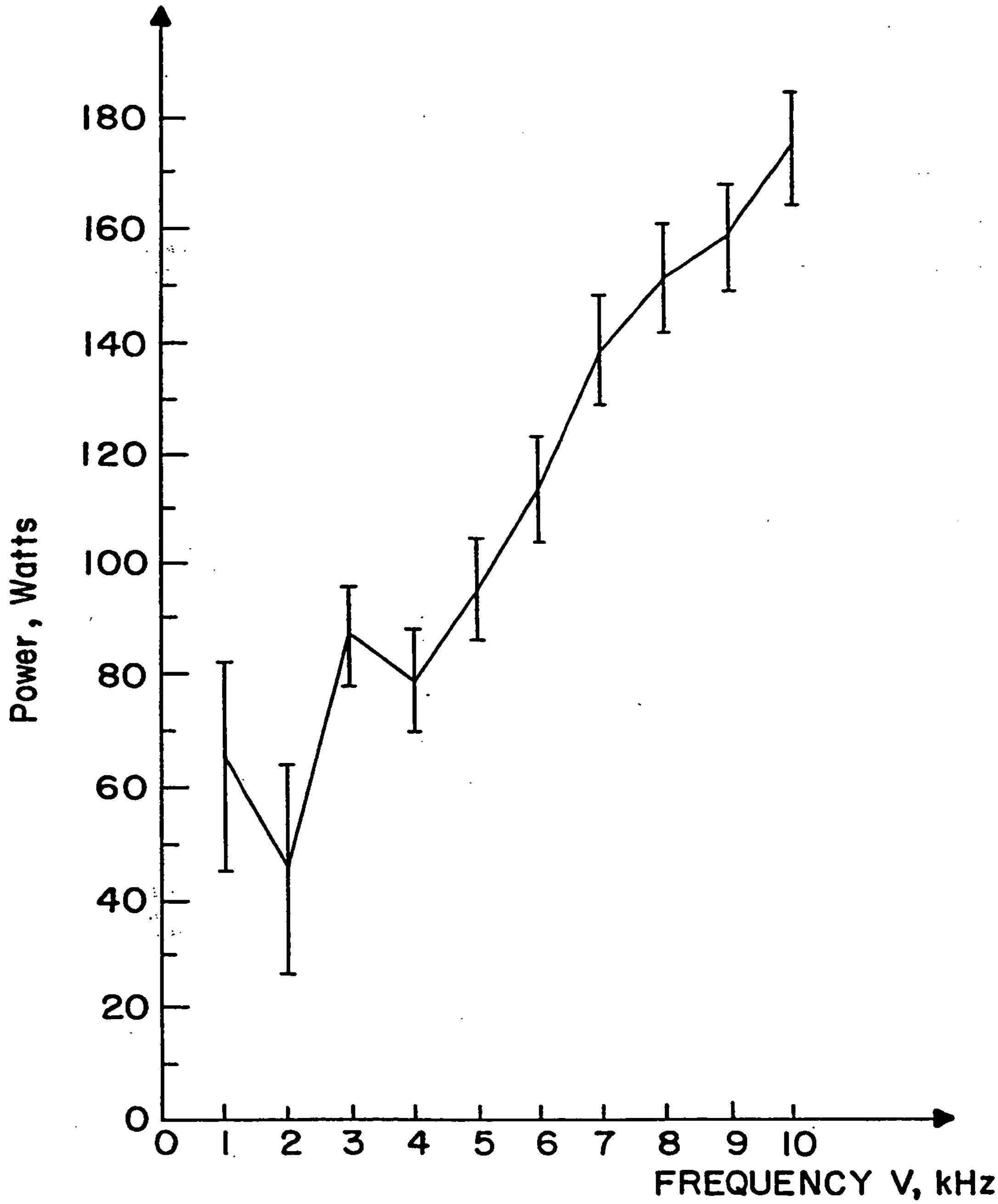

100°
80°
60°
40°
20°
10°
8°
6°
4°
2°
1°
Breakdown Phase Angle, ° Degrees
2
4
6
8
10
20
30
40
60
80
100
FREQUENCY, kHz

FIG. 13 12/12


180
160
140
120
100
80
60
40
20
0
Power, Watts
0 1 2 3 4 5 6 7 8 9 10
FREQUENCY V, kHz

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06151

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :H01J 7/24; H05B 31/26; D04H 1/58;
US CL :315/111.21, 111.51; 118/723E, 723I; 204/298.04; 428/288; 204/164
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 315/111.21, 111.51; 118/723E, 723I; 204/298.04; 428/224, 288, 903; 429/247, 249, 250; 204/164

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP,02,312,223(Koga) 27 December 1990, abstract.	1-13
Y	JP, 61-177374(Shimadzu) 30 January 1985, abstract.	1-13
Y	JP, 58-200529(Kubonai) 22 November 1983, abstract.	1-13
Y	Second Annual TANDEC Conference, Rakowski, Witold, "Effect and Cost of Plasma Treatment of Melt Blown Polymer Webs", 13-16 October 1992, p.11, l.22+; p.18, lines 5+.	14-24
A, P	US, A, 5,270, 137(Kubota) 14 December 1993, the entire document.	14-24

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 22 AUGUST 1994	Date of mailing of the international search report 30 AUG 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. N/A	Authorized officer Darius Gambino Telephone No. (703) 308-4090

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06151

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,147,493(Nishimura et al.) 15 September 1992, figs. 1-2.	1-13

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group I Claims 1-13 drawn to a plasma device classified in 315/111.51
Group II. Claims 14-24 drawn to a chemical web classified in 428/288
The claims of these two groups are directed to different inventions which are not linked to form a single general concept. The claims in the different groups do not have in common the same or corresponding "special technical features". In particular the chemical web of Group II is different from the plasma device described in Group I.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.